

Chapter 14

AQUEOUS REACTIONS, Part 4

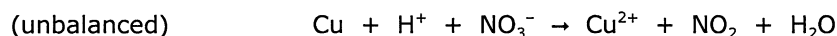
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We will now go into balancing redox equations. This is another case where several methods exist and different instructors may present different forms of them. I will describe one method; your instructor may present another method. Be aware of what you need to do.

14.1 Some preliminaries

Unfortunately, the variations for redox involve more than just the balancing methods. There are additional variations with how redox equations are actually presented as problems to students. Let me illustrate with one of the reactions by which copper metal dissolves in nitric acid. I'll present it to you in three ways, representing the most common problem types which many instructors and/or other resources use.

- Problem Type 1. "Balance the following equation."



- Problem Type 2. "Balance the following equation."



- Problem Type 3. "Balance the following equation in acidic solution."

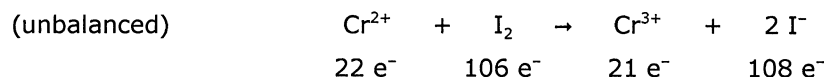


I am only going to work with one of these here, and that will be Type 1. This Type involves the net ionic format with all of the reagents provided in the given information. Your instructor may instead work with Problem Type 2 or 3. Problem Type 2 deals with the undissociated format instead of the net ionic equation. Problem Type 3 involves working with the net ionic equation but some reactants and products are not in the given information; this leaves the student to determine the missing reagents. We will actually deal with Problem Type 3 starting in Chapter 61, but that's then and not now. If your instructor is working with Problem Type 2 or Type 3 or even some other kind at this time, then the approach may differ from the one here. Although their approach may look different, I will tell you what really matters: the key to balancing redox is electron balance and the key to electron balance is to get the number of electrons lost equal to the number of electrons gained. It doesn't matter how it's taught or if there are twenty more variations. This is the important part. Let me say it again.

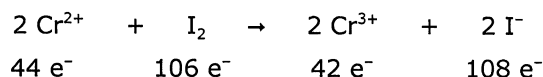
THE KEY TO BALANCING REDOX IS ELECTRON BALANCE AND THE KEY TO ELECTRON BALANCE IS TO GET THE NUMBER OF ELECTRONS LOST EQUAL TO THE NUMBER OF ELECTRONS GAINED.

Once you achieve electron balance, the rest of balancing will be much easier.

I will use our example from the end of the last Chapter to illustrate this point. Our first step was to place a coefficient of two on I^- which was wrong if you ended there.



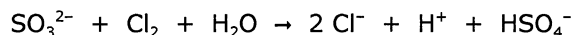
The reason that it was wrong was because the electrons did not balance. The reason the electrons did not balance was because the loss did not equal the gain. Notice in the reaction that the chromium loses one electron but the iodines gain two electrons total. That's no good. LOSS MUST EQUAL GAIN. If loss does not equal gain, then the electrons won't balance and the charges won't balance. Now consider the right answer.



The chromiums together lose a total of two electrons. The iodines together gain a total of two electrons. Loss equals gain. That's the key.

One last thing before jumping into balancing redox. I need to introduce a new term: couple. A couple of what? No, no, not that kind of couple. A redox couple. A redox couple is a redox reactant/product relationship. An oxidant and its product are one couple. A reductant and its product are another couple. Sometimes this is evident in the equation itself, especially after you've done a bunch of them, but sometimes it's not. You can identify each couple by oxnos: a redox couple is that reactant

and that product which contain the atom(s) undergoing a change in oxnos. For example, in the equation above, $\text{Cr}^{2+}/\text{Cr}^{3+}$ is one redox couple; I_2/I^- is the other redox couple. Notice that each couple is comprised of one reactant and its product. Let me do another example, using the sulfite and chlorine reaction from the last Chapter.



For this reaction, $\text{SO}_3^{2-}/\text{HSO}_4^-$ is one couple and Cl_2/Cl^- is the other couple.

OK, we now move on to our method of balance. As I said upstairs, I am working here with Problem Type 1 which involves the net ionic format with all reagents in the provided information. The balancing method which I will cover at this time is called the oxnos method. There is another method based on half-reactions, and we will actually do this in Chapter 61 when we do Problem Type 3. Your instructor may pursue this method at this time, or even one of the combination methods which are available.

14.2 Oxnos method

As you might guess by the name, the oxnos method accomplishes redox balance by using oxidation numbers. The critical balance step, getting electron loss equal to electron gain, is executed using only the oxidation numbers of the redox atoms within the redox couples. We are able to do this because of the connection between oxidation number and electron count. I first pointed this out in Section 13.3.

“ The oxnos system is set up to reflect a count of electrons for an atom in any kind of chemical unit. Since redox involves a loss or gain of electrons, this loss or gain will show up as a change in electron count, which means that it will also show up as a change in oxidation number. Given this connection, we can analyze and even define redox in terms of oxidation numbers. ”

It boils down to this: the change in oxidation number equals the number of electrons which are lost or gained. In order to balance the equation, you have to get these numbers equal. Once you've got the loss equal to the gain, the balancing is much easier. In fact, as long as you have loss equal to gain, then atom balance will guarantee charge balance.

There are six Steps.

- Step 1. Assign oxidation numbers and identify the redox atoms.
You're looking for the specific atoms which change their oxidation number. Remember that some atom's ON goes up and some atom's ON goes down.
- Step 2. Atom-balance the redox atoms only.
Don't do everybody yet! Just balance the atom count for the redox atoms at this step.
- Step 3. For the redox atoms, find the total change in oxnos.
That's total change, meaning the change per atom times how many atoms.
- Step 4. Equalize the total changes, inserting coefficients into the equation as needed.
This Step assigns coefficients to the redox couples. This Step fulfills the absolutely necessary requirement to set loss equal to gain.
- Step 5. Balance all other atoms.
In this Step, do NOT touch the coefficients for the redox couples as determined in Step 4! Instead, balance all other atoms using coefficients as needed.
- Step 6. Verify the result.
Things can get tricky doing these, so it's always useful at the end to verify atom-balance and charge-balance and to look for anything else unusual.

Let's start in on a number of Examples.

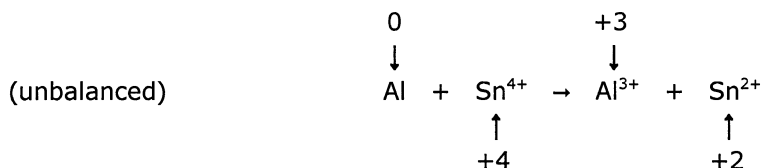
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Example 1. Balance the equation for the reaction of aluminum metal with tin(IV) ion, which produces aluminum ion and tin(II) ion.

From the names, you can write the following.



Notice that the atoms are balanced here, but the charges are not. A total of +4 is on the left but a total of +5 is on the right. That's no good. It's wrong. Let's fix this.

- Step 1. Assign oxidation numbers and identify the redox atoms.
The oxnos here are straightforward. For clarity, I'll show these for one couple above the equation and for the other couple below the equation.



- Step 2. Atom-balance the redox atoms only.
One aluminum each side, one tin each side. We're OK.
- Step 3. For the redox atoms, find the total change in oxnos.
The aluminum changes by three oxnos; one aluminum is present in the equation at this time.

$$\{\text{Al changes by 3 ON}\} \times \{1 \text{ Al present}\} = \{\text{total change of 3}\}$$

The tin changes by two oxnos; one tin is present in the equation.

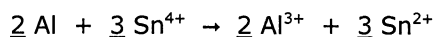
$$\{\text{Sn changes by 2 ON}\} \times \{1 \text{ Sn present}\} = \{\text{total change of 2}\}$$

- Step 4. Equalize the total changes, inserting coefficients into the equation as needed.
We have a total change by three and we have a total change by two; we introduce coefficients to bring them to the same number. We can bring both to six as follows.

Double the change of three by doubling the Al/Al³⁺ couple.

Triple the change of two by tripling the Sn⁴⁺/Sn²⁺ couple.

This gives us



Now, the total change for Al is

$$\{\text{each Al changes by 3 ON}\} \times \{2 \text{ Al present}\} = \{\text{total change of 6}\}$$

and total change for Sn is

$$\{\text{each Sn changes by 2 ON}\} \times \{3 \text{ Sn present}\} = \{\text{total change of 6}\}$$

The total changes are now equal at 6. Loss now equals gain. Why did I choose six? For this problem, six is the smallest number which you could get them both to equal without using fractional coefficients.

- Step 5. Balance all other atoms.
There aren't any others in this example.
- Step 6. Verify the result.

Two aluminums each side, three tins each side, +12 each side. All is groovy. You're done.

There are several points to note.

We went through this whole balance bit without saying who's losing, who's gaining, who's oxidizing whom, etc. All of these things are readily determined using the links between oxnos and electron count which were described in the last Chapter. Those are the key points which you circled at that time. For this problem, we can see the following.

Aluminum's ON is increasing, going positive. An increasing ON means Al is losing negative electrons.

Therefore, this is oxidation.

Tin(IV)'s ON is decreasing, going less positive. A decreasing ON means Sn(IV) is gaining negative electrons. Therefore, this is reduction.

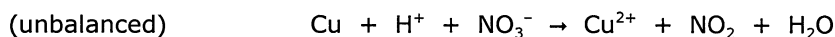
Al is the reductant. Sn⁴⁺ is the oxidant.

Al reduces Sn⁴⁺. Sn⁴⁺ oxidizes Al.

If you can't understand how each of those phrases applies to this problem, stop and go back to the parts in Chapter 13 dealing with those terms.

Let's go to another Example, the Chapter opener.

Example 2. Balance the following equation.



Let me expand on this a bit first. Here is the equation with phases, for illustration purposes.

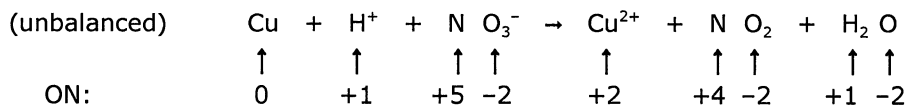


The reaction of copper with nitric acid can actually involve other equations also but we'll just work with this one. These reactions are typical of how various metals dissolve in nitric acid. When NO_2 is a product, it is obvious. Nitrogen dioxide is a gas. It's also a very nice orange color. There are not many colored gases and many people are not familiar with the notion that a gas can have a color, but some do. When you have a reaction which produces nitrogen dioxide, orange gas billows out of the solution. If there's a lot of it, it may appear brown. Although it may be pleasant to see, you don't want to breathe the stuff. It's very corrosive and very toxic.

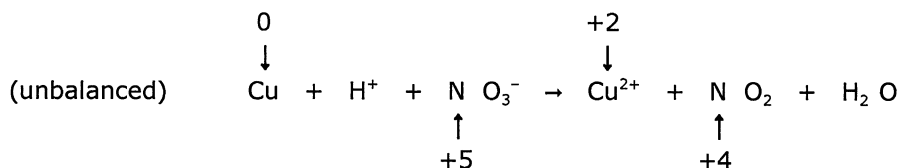
Let's start on balancing this equation.

- Step 1. Assign oxidation numbers and identify the redox atoms.

There're lots of things in this equation. I'll just go ahead and show all the oxidation numbers.



Notice that the copper and the nitrogen are changing oxnos; this identifies them as the redox atoms. The redox couples are Cu/Cu^{2+} and $\text{NO}_3^-/\text{NO}_2$. After identifying the redox atoms, only the oxnos for the redox atoms really matter. I'll rewrite this for clarity.



- Step 2. Atom-balance the redox atoms only.

There are one copper on each side and one nitrogen on each side. Fine. Leave them as is.

- Step 3. For the redox atoms, find the total change in oxnos.

The copper changes by two oxnos; one copper is present in the equation at this time.

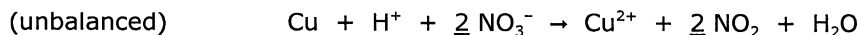
$$\{\text{Cu changes by 2 ON}\} \times \{1 \text{ Cu present}\} = \{\text{total change of 2}\}$$

The nitrogen changes by one oxidation number. One nitrogen is present in the equation.

$$\{\text{N changes by 1 ON}\} \times \{1 \text{ N present}\} = \{\text{total change of 1}\}$$

- Step 4. Equalize the total changes, inserting coefficients into the equation as needed.

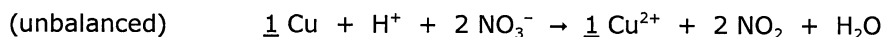
We have to get a total change of two equal to a total change of one: we will double the change of one. We do this by multiplying the $\text{NO}_3^-/\text{NO}_2$ couple by two.



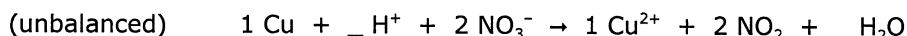
Now, N has a total change of two ($1 \times 2 = 2$), and this is equal to the total change for Cu. Loss and gain are now equal.

- Step 5. Balance all other atoms.

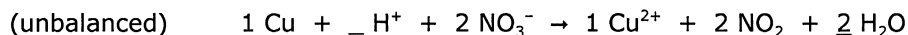
In this Step, you cannot touch the coefficients for the redox couples. The coefficients of two on NO_3^- and on NO_2 are fixed, and so also are the coefficients of one for Cu and Cu^{2+} . Go ahead and write in the ones if you wish.



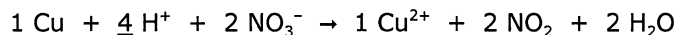
You can only change the coefficients for H^+ and H_2O . We'll focus on these.



These last two coefficients are determined by the H and O counts. The O count has already been decided: on the left side, the two nitrates provide six O's; therefore, six O's must be present on the right. Four of those six are within the nitrogen dioxides; you need two more from H₂O. This means we must insert a coefficient of two for H₂O.

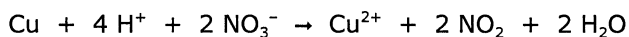


This now determines the fate for the H's. The right side is fixed at four hydrogens total, so that requires four hydrogens on the left.



- Step 6. Verify the result.

One copper each side. Four hydrogens each side. Two nitrogens each side. Six oxygens each side. +2 on the left, +2 on the right. Frabjous! Notice that, once you have loss equal to gain, then atom balance guarantees charge balance. Now, go ahead and clear the 1's.



We see from all of this that:

Copper's ON is increasing, going positive. An increasing ON means Cu is losing negative electrons. Therefore, this is oxidation.

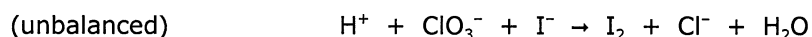
Nitrogen's ON is decreasing, going less positive. A decreasing ON means N is gaining negative electrons. Therefore, this is reduction.

Cu is the reductant. NO₃⁻ is the oxidant.

Cu reduces NO₃⁻. NO₃⁻ oxidizes Cu.

We'll do a third Example, but this one has a twist.

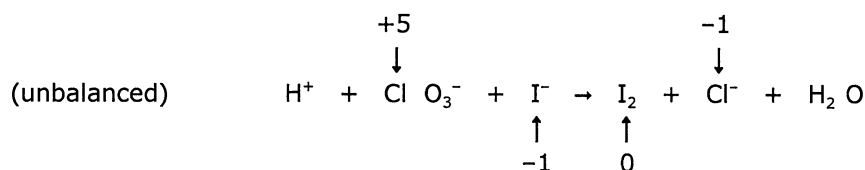
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Example 3. Balance the equation for the oxidation of iodide by chlorate. Or is it the reduction of chlorate by iodide? It's both.



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 Jump right in.

- Step 1. Assign oxidation numbers and identify the redox atoms.

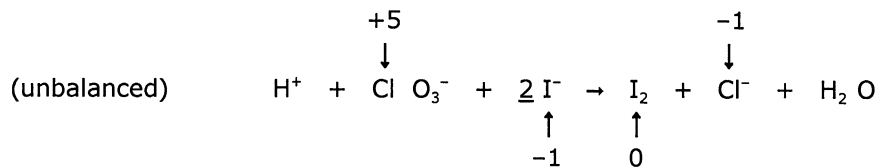
I won't spell all of these out, but I'll summarize them. All H's are +1; they're not changing oxnos so they're not the redox atoms here. All O's are -2, so they're not the redox atoms either. As you may have realized from the description anyway, the chlorines and the iodines are the atoms undergoing redox.



The couples are ClO₃⁻/Cl⁻ and I⁻/I₂.

- Step 2. Atom-balance the redox atoms only.

There's one chlorine on each side, which is fine. However, the iodine count is off: we need a coefficient of two on iodide ion.



Our prior two Examples didn't need anything in this step. I picked this problem to show you this variation.

- Step 3. For the redox atoms, find the total change in oxnos.

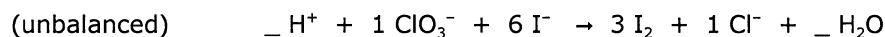
The chlorine changes by six oxnos. (If you think it should be four, watch the signs.) One chlorine is given by the equation, so the total change for chlorine is $6 \times 1 = 6$. Each iodine changes by one oxnos; since there are TWO iodines, the total change for the iodines is $1 \times 2 = 2$.

- Step 4. Equalize the total changes, inserting coefficients into the equation as needed. We have to get a total change of six equal to a total change of two. We triple the two by tripling the I^-/I_2 couple. Notice that there's a prior coefficient of two on the iodide; that also triples.

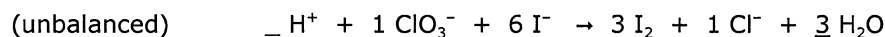


Loss now equals gain: the chlorines and the iodines both have a total change of six.

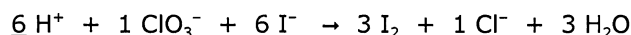
- Step 5. Balance all other atoms. There are six reagents in the equation and four of the coefficients were determined in Step 4. You cannot touch those four coefficients in this Step. You have only the coefficients for H^+ and H_2O to play with.



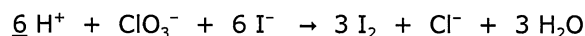
The oxygen count has already been determined on the left: there are three, so there have to be three on the right. That means water gets a three.



That establishes six hydrogens on the right, so we need six hydrogens on the left.



- Step 6. Verify the result. Six hydrogens each side. One chlorine each side. Three oxygens each side. Six iodines each side. Total charges -1 both sides. Clear your 1's and you're done.



Getting the hang of it?

I'll bring in some Pointers here which will assist in many cases in Step 1, since assigning oxnos for everything can take a while. For purposes of Step 1, look for the following types of reagents first, on either side of the unbalanced equation. (They don't have to be on both sides.) If present, see if the atoms involved are changing oxidation number.

- ☞ A. Elemental forms
Al in Example 1, Cu in Example 2, and I_2 in Example 3 were all elemental forms; all were changing ON.
- ☞ B. Monatomic ions
 Al^{3+} , Sn^{4+} and Sn^{2+} in Example 1, Cu^{2+} in Example 2, and I^- and Cl^- in Example 3 were all monatomic ions; all were changing ON. (Keep in mind that H^+ is not a monatomic ion, so it is not in this pointer.)
- ☞ C. Oxyanions or oxyacids: check the element other than oxygen.
 NO_3^- in Example 2 and ClO_3^- in Example 3 were both oxyanions; N and Cl were changing ON.

These Pointers are clues but not guarantees. They don't cover every possibility but they are very good for where we are at now. Also for where we are at now, I will add a simplifying practice: for balancing redox equations, all H's will be $+1$ and all O's will be -2 EXCEPT when they are given as elemental forms (Pointer A). All H's and all O's in Examples 2 and 3 followed this. But note that, like always, your instructor can modify any of this for their purposes. We will be changing some of this in Chapter 61 anyway.

Sally forth!

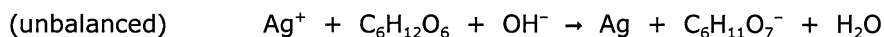
14.3 It's your turn.

Let's consider the redox equation for the "silver mirror" reaction. What's a "silver mirror" reaction? It's an example of "chemical plating", which involves plating some metal onto a surface by a chemical reaction. ("Electroplating" is another plating method but it uses electricity. We'll discuss this in Chapter 65.) Here's the general gist for the "silver mirror" as done in a popular demonstration. You begin with two solutions: one contains silver nitrate in a basic solution and the other contains glucose, $C_6H_{12}O_6$. Both

solutions are clear and colorless to start. You add the two together in a glass container and things get dark. Within minutes the surface of the glass becomes coated with a shiny plating of elemental silver metal. This is actually a mirror on the inside surface of the container. This reaction has been known for a long time and variations of it have been used to make mirrors for many years, although nowadays different techniques are available. Why would you want to put a mirror inside a glass container? They're used for temperature insulation in glass vacuum bottles, in the laboratory and also in your home. For many decades, glass vacuum bottles were the heart of thermos-type containers; these involved a double-walled glass liner with a silver mirror on the inside of the glass walls. The thermos-type bottles are nowadays primarily stainless steel or plastic, but a glass version can still be found periodically. Although typical consumer use has dwindled over the years, laboratory uses are still plentiful, especially with ultra-cold liquids such as liquid nitrogen ($-196\text{ }^{\circ}\text{C}$).

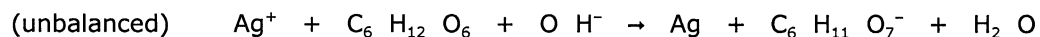
Let's go ahead and get started. I've already mentioned many of the reagents in the equation, but not all. The glucose can react to give several products but I'll stick with one, $\text{C}_6\text{H}_{11}\text{O}_7^-$. That identifies one couple as $\text{C}_6\text{H}_{12}\text{O}_6/\text{C}_6\text{H}_{11}\text{O}_7^-$. From the description provided, you may see that silver metal is produced from the silver ion in silver nitrate; that's the other couple, Ag^+/Ag . Hydroxide is another reactant and water is another product.

Example 4. Balance the following equation.



Go ahead. Start filling in.

- Step 1. Assign oxidation numbers and identify the redox atoms.
One couple will be readily identified by the prior Pointers. The other isn't covered by the Pointers.



- Step 2. Atom-balance the redox atoms only.

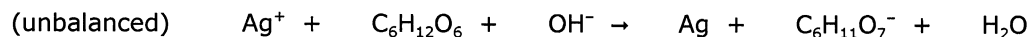


- Step 3. For the redox atoms, find the total change in oxnos.
(Clue: somebody has a fractional oxnos. Watch your math.)

The total change for the Ag/Ag^+ couple is _____.

The total change for the $\text{C}_6\text{H}_{12}\text{O}_6/\text{C}_6\text{H}_{11}\text{O}_7^-$ couple is _____.

- Step 4. Equalize the total changes, inserting coefficients into the equation as needed.



- Step 5. Balance all other atoms.

Only the coefficients for OH^- and for H_2O should remain by now. This Step is not as easy for this problem as it was for the previous examples. Let me throw in another clue. You already set the loss equal to the gain in Step 4. This allows you to use charge balance to help with the remaining atom balance. Here's how that works. The total charges on the right side will be determined only by the coefficient which you assigned to $\text{C}_6\text{H}_{11}\text{O}_7^-$. The total charges on the right side must equal the total charges on the left side; from that and from the coefficient on Ag^+ , find the coefficient for hydroxide. Once you do that, then only the coefficient for H_2O remains; you can find that one from the H or O counts.

- Step 6. Verify the result.

Be sure to check that everything is OK. If you want to check your final answer, the coefficients are 1, 1, 2, 2, 2, and 3, but not in that order. By the way, the use of charge balance in Step 5 could have been done in the earlier Examples, but it wasn't really necessary. It is a very handy thing to keep in mind, though.

From these Examples, I hope you are catching on to the process. It will take practice. I'll give you three more equations to balance, but I won't work you through the Steps this time.

.....
Example 5. Balance the following equations.

- A. (unbalanced) $\text{Se} + \text{Pb}^{4+} + \text{H}_2\text{O} \rightarrow \text{Pb}^{2+} + \text{SeO}_3^{2-} + \text{H}^+$
 B. (unbalanced) $\text{SO}_3^{2-} + \text{SbO}_2^- + \text{H}_2\text{O} \rightarrow \text{S}_2\text{O}_3^{2-} + \text{SbO}_3^- + \text{OH}^-$
 C. (unbalanced) $\text{WO}_2 + \text{ReO}_4^- + \text{H}^+ \rightarrow \text{W}_2\text{O}_5 + \text{Re} + \text{H}_2\text{O}$

Here's some space.

- A. (unbalanced) $\text{Se} + \text{Pb}^{4+} + \text{H}_2\text{O} \rightarrow \text{Pb}^{2+} + \text{SeO}_3^{2-} + \text{H}^+$
 B. (unbalanced) $\text{SO}_3^{2-} + \text{SbO}_2^- + \text{H}_2\text{O} \rightarrow \text{S}_2\text{O}_3^{2-} + \text{SbO}_3^- + \text{OH}^-$
 C. (unbalanced) $\text{WO}_2 + \text{ReO}_4^- + \text{H}^+ \rightarrow \text{W}_2\text{O}_5 + \text{Re} + \text{H}_2\text{O}$

If you have troubles with these, review the Examples done previously. There're many similarities. Again, if you'd like to check your answers, the coefficients for equation A are 1, 1, 2, 2, 3, and 6, but not in that order. The coefficients for equation B are 1, 1, 2, 2, 2 and 2, but not in that order. (You might want to use the charge balance trick as explained in Step 5 of Example 4.) The coefficients for equation C are 1, 2, 2, 2, 7 and 14, but not in that order.

Redox reactions are all around you and they're incredibly important to a wide range of things. I mentioned in Chapter 13 that combustion is redox. I mentioned in Chapter 6 that the foods you eat undergo combustion. Fats, carbohydrates and proteins ultimately serve as reducing agents (although some have other operational roles before being combusted). For humans, O_2 is the ultimate oxidant and that is why you breathe. Redox powers your body. In fact, redox powers all forms of life. The ultimate reductant and the ultimate oxidant can vary, especially for the vast range of microcritters on the planet: for example, some use H_2 as reductant, some use SO_4^{2-} as oxidant, etc. You also use redox in other applications of your everyday world; for example, every time you use a battery, you're using redox. Most batteries no longer involve aqueous solutions, although this is how they originally developed. Many batteries nowadays use pastes instead of aqueous solutions. Nevertheless, there is one battery which is still very common and which still uses aqueous solutions: the standard lead-acid battery in cars and in other applications. Regardless of type, all batteries use redox reactions. The trick is to design the reaction so that the oxidant has to work for the electrons. This is accomplished by physically separating the oxidant and reductant within the battery cell. Under this setup, the oxidant must now pull the electrons through a circuit, thereby lighting your lights, playing your music, and starting your engine. These things are part of your world. A REALLY BIG part. We'll see more of how this happens starting in Chapter 61.

Problems

1. Balance the following equations. All reactants and products are shown.
 - a. $\text{H}_3\text{PO}_2 + \text{Ni}^{2+} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_4 + \text{Ni} + \text{H}^+$
 - b. $\text{H}_2\text{O} + \text{Sn} + \text{OH}^- + \text{N}_2 \rightarrow \text{HSnO}_2^- + \text{NH}_3$
 - c. $\text{PbO}_2 + \text{VO}^{2+} + \text{OH}^- \rightarrow \text{PbO} + \text{V}_2\text{O}_5 + \text{H}_2\text{O}$
 - d. $\text{HNO}_2 + \text{H}^+ + \text{Cl}^- \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} + \text{HClO}$
2. Balance the following equations. All reactants and products are shown.
 - a. $\text{Au}^+ + \text{NO}_2^- + \text{H}_2\text{O} \rightarrow \text{Au} + \text{NO}_3^- + \text{H}^+$
 - b. $\text{S}_2\text{O}_6^{2-} + \text{H}_2\text{O} + \text{IO}^- \rightarrow \text{SO}_2 + \text{IO}_3^- + \text{OH}^-$
 - c. $\text{BrO}_3^- + \text{OH}^- + \text{Zn} \rightarrow \text{Br}_2 + \text{H}_2\text{O} + \text{ZnO}_2^{2-}$
 - d. $\text{OH}^- + \text{NiO}_2 + \text{Cr}(\text{OH})_3 \rightarrow \text{Ni}(\text{OH})_2 + \text{CrO}_4^{2-} + \text{H}_2\text{O}$
3. Each of the following equations is balanced. Identify the redox couples. Also, for each reaction as written, how many electrons are transferred (lost or gained)?
 - a. $\text{H}_2\text{C}_2\text{O}_4 + \text{Hg}^{2+} \rightarrow \text{Hg} + 2 \text{CO}_2 + 2 \text{H}^+$
 - b. $2 \text{MnO}_4^- + 8 \text{H}^+ + 3 \text{I}^- \rightarrow 2 \text{MnO}_2 + 4 \text{H}_2\text{O} + 3 \text{I}_2$
 - c. $2 \text{Sb} + 3 \text{H}_5\text{IO}_6 \rightarrow 2 \text{SbO}^+ + \text{H}^+ + 3 \text{IO}_3^- + 7 \text{H}_2\text{O}$